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CHEMICAL ANALYSIS OF TEN CLAYS AND SHALES FROM ONTARIO

by

D.J. Charette, J.C. Hole and E. Mark

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INTRODUCTION

The non-metallic mineral laboratories of the Mineral Sciences Division have been collaborating with the Mineral Processing Division for several years in a program of determining the chemical composition and physical properties of those Canadian clay and shale deposits of economic interest.

In the initial stages of this program about 80 deposits in various parts of Canada were investigated. The present phase covers some Ontario deposits overlooked in the first survey. This report gives the chemical analyses of 10 clays and shales sampled from deposits throughout this province.

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ANALYTICAL METHODS

SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, FeO, Fe_2O_3, TiO_2, Quartz, H_2O + 105°C, H_2O - 105°C, CO_2, Total Carbon, S, and Organic Carbon.

Silica (SiO_2)

Fusion with sodium carbonate flux is followed by double dehydration with perchloric acid.

Alumina (Al_2O_3), Lime (CaO) and Magnesia (MgO)

A separate sample is taken into solution by acid treatment (hydrofluoric, hydrochloric and sulphuric) and evaporated to fumes several times to volatilize the fluoride. It is then transferred to a 500-ml separatory funnel and the acid concentration adjusted to approximately 10 per cent v/v sulphuric acid. Sufficient 9 per cent cold cupferron solution is added to the cooled solution (15°C) to precipitate the iron, titanium etc. The precipitated cupferrates are extracted with several portions of cooled chloroform.

The aqueous phase is then returned to a beaker, a small amount of nitric acid added and the solution evaporated to fumes to destroy any residual cupferron.

The solution is then diluted, heated to boiling and the Al_2O_3, CaO and MgO determined by the usual classical procedures employing double precipitations in all cases.

Soda (Na_2O) and Potassia (K_2O)

These two constituents are determined by the flame photometric procedure as described in Mines Branch Technical Bulletin TB 24 (1).

Ferrous Oxide (FeO)

A sample is decomposed under an inert atmosphere with hydrochloric and hydrofluoric acids. When decomposition is complete the solution is transferred to a saturated solution of boric acid then titrated in the usual manner with potassium dichromate solution using sodium diphenylamine as an indicator.

In the case where organic material is present in considerable amounts the results for ferrous oxide may be slightly high. In some cases the end point is obscured by highly coloured organic matter.

Ferric Oxide (Fe_2O_3) and Titania (TiO_2)

A sample is decomposed by acid treatment using hydrofluoric, hydrochloric and sulphuric acids, evaporated to SO_3 fumes several times to volatize fluoride, transferred to a 100-ml volumetric flask and diluted to volume.

Appropriate aliquots are taken to determine iron spectrophotometrically by the ferrous-phenanthroline complex and titanium by the peroxy-titanium method.

Ferric oxide is calculated by subtracting the ferrous iron from the total iron value.

If iron is known to be high, it should be determined on a separate sample by a volumetric procedure. If titania is low, it should also be

determined on a separate sample using the same method (Spectrophotometric with peroxide).

Quartz

Quartz is determined by the method of L.J. Trostel and D.J. Wynne (2).

Water + 105°C

A sample, dried at 105°C, is burned at approximately 900°C in a Vitreosil combustion tube fitted in a Leco furnace. A flow of dried oxygen is passed through the tube then through a water absorption tower that has been properly "blanked". The sample may be used as received and the total water value, so obtained, corrected for the -105°C water which is determined at approximately the same time.

Water -105°C

A sample is transferred to a tared platinum dish and placed in a warming oven, set at 105°C, for one hour. The dish is then removed, cooled in a desiccator and reweighed. The difference (loss in weight) is reported as per cent water -105°C.

Carbon Dioxide (CO_2)

A sample is transferred to a flask connected to an air-tight absorption train. The sample is decomposed with perchloric acid and boiled to remove the CO_2 from the solution. A current of air is passed through the system carrying with it the CO_2. The CO_2 absorption tower is disconnected, cooled and weighed. The increase in weight over a blank run is reported as per cent CO_2.

Total Carbon (C) and Sulphur (S)

These two constituents are determined by combustion technique using a Leco combustion furnace fitted with mullite combustion tubes. A current of oxygen, passed through water and carbon dioxide absorption towers is swept through the combustion tube carrying the liberated SO_2 or CO_2 with it.

For total carbon the gas is passed through an absorption train containing a "blanked" CO_2 absorption tower.

For sulphur the SO_2 gas is bubbled through a silver nitrate solution containing an acid-base indicator. Silver sulphite is precipitated and the liberated nitric acid is titrated with standard sodium hydroxide solution. Suitable standards are necessary for calibration.

Elemental and Organic Carbon

Elemental and Organic Carbon is calculated by subtracting the CO_2 carbon from the total carbon.

REFERENCES

1. Elsie M. Penner and W.R. Inman, "Flame photometric methods used in the Mineral Sciences Division, Mines Branch, Ottawa", TB 24 (1961).

2. L.J. Trostel and D.J. Wynne, "Determination of Quartz (Free Silica) in Refractory Clays". J. Amer. Ceram. Soc. 23, 18, (1940).

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DJC:JCH:EM:ST

TABLE I

Results of Tests on 10 Clay Samples from Ontario (a)

Lab. No.	Sample No.	SiO_2	FeO	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	Total C	Elemental & Organic C (calculated)	S	L.O.I.	H_2O -105°C	H_2O +105°C	CO_2	Quartz	Na_2O	K_2O	Totals
5133	U-218	38.52	1.83	3.85	0.63	13.08	15.10	5.33	3.97	0.03	0.028	18.01	0.39	3.47	14.44	9.90	0.12	3.89	100.26
5134	U-220	67.60	1.06	4.50	0.76	14.72	0.81	1.60	0.85	0.74	0.033	5.52	1.52	4.32	0.42	39.67	0.68	3.16	99.63
5135	U-460	48.36	1.95	4.38	0.78	14.28	9.29	4.07	2.33	0.01	0.023	12.10	0.58	3.59	8.52	19.62	0.12	4.30	99.64
5136	U-471	59.92	1.77	4.06	0.76	15.02	4.94	3.41	0.75	0.10	0.019	4.70	1.42	2.08	2.40	32.92	2.60	3.15	100.11
5137	U-584	64.00	1.25	4.14	0.52	16.15	2.23	2.07	0.95	(b)	(b)	4.61	1.69	3.96	(b)	34.94	2.65	2.60	100.25
5138	U-939	55.56	0.15	4.22	1.23	27.54	0.26	0.20	0.14	0.08	<0.015	10.50	0.50	10.61	0.22	22.49	0.04	0.16	100.19
5139	U-942	62.72	2.18	9.32	0.83	15.00	0.12	1.25	0.48	0.17	0.029	6.76	0.75	5.50	1.16	23.81	0.09	2.22	100.47
5140	U-1053	63.72	1.16	4.52	0.67	16.06	1.58	2.28	0.60	0.55	0.019	4.60	1.38	3.30	0.17	36.17	2.40	3.30	100.31
5141	U-1054	65.12	1.77	3.60	0.63	15.12	1.75	2.72	0.22	0.21	<0.015	3.57	1.19	3.03	0.01	39.16	2.33	2.97	99.58
5142(d)	U-1056	56.76	2.06	4.05	0.81	13.80	0.52	1.57	7.48	7.36	2.75 (c)	15.70	0.71	9.20	0.44	31.40	0.52	3.26	99.05

(a) Analysis done on a dry basis.
(b) Insufficient sample supplied for determination.
(c) Duplicate determinations.
(d) Total Fe as Fe_2O_3 = 6.33. Sample too black for clear FeO end-point.